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The impact of anthropogenic chlorine emissions, stratospheric ozone change and chemical feedbacks on stratospheric water

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Abstract. Mixing ratios of water (H_2O) in the stratosphere appear to increase due to increased input of H_2O and methane from the troposphere and due to intensified oxidation of CH_4 in the stratosphere, but many of the underlying mechanisms are not yet understood. Here we identify and quantify three chemical mechanisms which must have led to more efficient oxidation of CH_4 in the stratosphere over the past several decades: 1) The increase in stratospheric chlorine levels due to anthropogenic CFC emissions, 2) the thinning of the stratospheric ozone column and 3) enhanced OH levels in the stratosphere due to increasing H_2O levels themselves. In combination with the increase in tropospheric CH_4 mixing ratios and with solar cycle related variations of upper stratospheric ozone, these effects can explain about 50% of the additional conversion of CH_4 to H_2O as observed throughout the stratosphere. The relative contributions from the individual processes have varied over the past decades.

1 Introduction

The observed increase of water vapour mixing ratios in the stratosphere (Oltmans and Hofmann, 1995; Oltmans et al., 2000; SPARC, 2000; Rosenlof et al., 2001) has received considerable attention because of its importance for the earth's radiative balance (Forster and Shine, 2002). Furthermore, an increase in stratospheric water vapour will have direct impact on stratospheric ozone chemistry (Kirk-Davidoff et al., 1999; Dvortsov and Solomon, 2001). Understanding this increase represents one of the great challenges in present atmospheric research. The collective evidence from numerous in situ and remote sensing measurement series of stratospheric water vapour suggests a positive trend of roughly 0.45%/yr (Rosenlof et al., 2001), which may have persisted for about

45 years, if the earliest measurements are reliable. Additional insight can be gained from measurements of CH_4 , because CH_4 oxidation is the only substantial in situ source of water in the stratosphere. This means that once an air parcel has entered the stratosphere, its H_2O mixing ratio gradually increases as CH_4 is oxidized. Since two water molecules are formed for each CH_4 molecule destroyed, the quantity $\text{H}_2\text{O}+2\times\text{CH}_4$ is conserved in the stratosphere, if the mixing ratio of the third hydrogen reservoir, H_2 , does not change (Jones et al., 1986).

Global remote sensing observations of H_2O and CH_4 from the Halogen Occultation Experiment (HALOE) from 1992 to 1997 (Randel et al., 1999) revealed two separate features at different altitudes in the stratosphere: 1) a uniform positive trend of $\text{H}_2\text{O}+2\times\text{CH}_4$ throughout the stratosphere above 25 km, that is likely due to increasing input of water from the troposphere (Zhou et al., 2001; Rosenlof, 2002; Sherwood, 2002) and 2) superimposed a H_2O trend which gradually increases with altitude, accompanied by a gradually decreasing trend in methane mixing ratios, which even turns negative at altitudes above about 30 km (Fig. 6 in Randel et al., 1999). Thus, although CH_4 mixing ratios were increasing in the troposphere (Blake and Rowland, 1988; Dlugokencky et al., 2001; Simpson et al., 2001) they were actually decreasing in the middle and upper stratosphere.

This observation indicates that the efficiency of the conversion of CH_4 into H_2O has increased over the considered time period, however, the reasons for this more efficient CH_4 oxidation are not fully understood. Nedoluha et al. (1998) carried out model calculations and concluded that the stratospheric CH_4 trends could be explained by changes in the vertical transport rate in the tropics. Considine et al. (2001) showed that the disturbance of stratospheric circulation patterns by the eruption of Mount Pinatubo in 1991 might have contributed to, but could not fully account for the observed changes in stratospheric CH_4 . Rosenlof (2002) recently suggested that changes in the residual circulation can lead to

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increased residence times of CH₄ in the stratosphere and thus may contribute to an intensified conversion to H₂O. Here we show that in addition to dynamical mechanisms an increased oxidation of CH₄ by Cl, O(¹D) and OH radicals must have caused a more efficient conversion of CH₄ to H₂O in the past decades, and that this mechanism has contributed significantly to the observed H₂O trends in the middle and upper stratosphere.

2 Stratospheric in situ production of H₂O

The relative strengths of the three CH₄ sink processes, reaction with Cl, O(¹D) and OH, can be obtained from CH₄ isotope measurements, because all three reactions are associated with different isotope fractionations. Recent measurements of the heavy isotope content of stratospheric CH₄ are reproduced well in atmospheric models when the relative share of the Cl-based stratospheric CH₄ sink is 20 to 35% (Saueressig et al., 2001; McCarthy et al., 2003; Rice et al., 2003). Thus, the reaction with Cl is an important sink of CH₄ in the present day stratosphere. The history of the atmospheric chlorine burden and its increase due to anthropogenic CFC emissions in the second half of the 20th century is well established (Butler et al., 1999; WMO, 2003). An increase of atmospheric CFC levels must inevitably lead to an increased Cl-driven sink of stratospheric CH₄. Thus, the conversion of CH₄ to H₂O will become more efficient, which should lead to an increase in stratospheric H₂O levels at a given altitude.

The most important consequence of anthropogenic CFC emissions was the chlorine catalyzed destruction of ozone in the stratosphere. In addition to the well-known dramatic destruction of stratospheric ozone in polar spring, publicly known as the “ozone hole”, ozone has also been reduced by anthropogenic chlorine on a global scale. Observations between 1979 and 1999 show that the decline of O₃ is altitude dependent and amounts to 3–6% per decade in the 40–50 km altitude range (WMO, 2003). In addition to destruction by Cl, upper stratospheric ozone is also affected by the solar cycle (WMO, 2003). A global ozone decrease in the upper stratosphere causes a further chemical feedback on stratospheric water vapour. The ozone photolysis rate $J(\text{O}_3)$ and thus the production rate of O(¹D) critically depends on the ozone column above the photolysis region. The thinning of the ozone column above increases the actinic flux available for the photochemistry of O₃ at a certain altitude and thus increases the O(¹D) production rate. More O(¹D) production means increased destruction of CH₄ and thus enhanced production of H₂O. Moreover, since OH in the stratosphere is primarily formed via



a higher O(¹D) concentration also means more OH production. Hence, the thinning of the upper stratospheric ozone

column must have caused an increase of O(¹D) and OH levels and thereby a more efficient conversion of CH₄ to H₂O.

According to reaction (1) the increase of water vapour levels in the stratosphere itself will also lead to a higher OH production rate. Thus both, the additional H₂O input from the troposphere, as well as the additional H₂O from more efficient CH₄ oxidation as just described, cause higher OH concentrations and in turn an intensified production of H₂O from CH₄.

In combination, the increase in anthropogenic CFC emissions, the variations in stratospheric ozone and the increased input of tropospheric water into the stratosphere must have caused a more efficient oxidation of CH₄ and thus production of H₂O in the stratosphere. We note that there are additional second order effects, e.g. the Cl- and O(¹D)-initiated removal of CH₄ will produce OH radicals further along the CH₄ oxidation sequence, which will not be discussed here.

3 Model calculations

We have carried out stratospheric model calculations to investigate these three effects in detail. Atmospheric models are available at various levels of complexity ranging from box models to high resolution 3-D models. Each of these model types has its particular strengths and weaknesses. For our study we use a chemical box model to focus on the chemical mechanisms that are put forward here. This model neglects atmospheric mixing effects but allows us to correctly describe the age of air in an air parcel rising in the stratosphere in the tropics, a quantity that is often not well reproduced in more complex models (Hall et al., 1999; WMO, 1999). A further advantage of using this box model is that the three effects can be assessed separately by individually including or neglecting the respective changes in the atmospheric composition, constrained by the available observations.

In addition, we have also carried out simulations with a two-dimensional model to investigate the impact of mixing and to examine the latitude dependence of the results. We emphasize again that 2-D (and 3-D) models generally underestimate the mean age of stratospheric air (Hall et al., 1999; WMO, 1999), i.e. they transport air too quickly through the stratosphere. Nevertheless, the results from the box model and from the 2-D model calculations, each having inherent advantages and deficiencies, provide a consistent picture, which gives us confidence that the results presented here are robust and are not dependent on a particular model.

Our box model consists of the chemistry module of the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002). Simulations are performed along an idealized trajectory for a single air parcel that rises from the tropical tropopause (15° N) to 1 hPa within 4 years, as deduced and extrapolated from observations of water vapour variations ascending in the tropical stratosphere (Mote et al.,

1996; Rosenlof, 2002). As mentioned above, atmospheric mixing is neglected in such box model calculations. This leads to altitude profiles of CH_4 mixing ratios that decrease too slowly in the lower stratosphere below about 10 hPa and too quickly above, when compared to stratospheric conditions, where mixing reduces the meridional gradients. Nevertheless, the total removal of CH_4 in the model is realistic, and half of the tropospheric CH_4 is decomposed at about 3 hPa, which is comparable to HALOE CH_4 observations.

Along the path of the considered air parcel the complete stratospheric photochemistry with 98 chemical and 36 photolysis reactions is simulated, including CH_4 oxidation and decomposition of CFCs and N_2O . Typical monthly temperature changes are included in the idealized trajectories. Abundances of the radical species Cl , OH and $\text{O}(^1\text{D})$ are calculated from their precursors (e.g. CFCs, O_3 or H_2O itself), using recommended photolysis and chemical rate coefficients (Sander et al., 2000). The air parcel is initialized with a chemical composition taken from simulations with the Mainz photochemical 2-D model (Gidel et al., 1983; Groöb, 1996). The underlying boundary conditions for all box and 2-D model simulations in this study are taken from the WMO scenarios (WMO, 1999; WMO, 2003). Based on these scenarios and the observed trends of water input from the troposphere into the stratosphere (SPARC, 2000; Rosenlof et al., 2001) we then varied for the considered time periods the initial CFC, H_2O and CH_4 content of the air parcel, as well as the ozone profile that was used in the radiative transfer code to determine the photolysis frequencies, to study the effects on stratospheric water vapour mixing ratios. This means that the temporal trends in radical abundances are wherever available based on observed trends of the precursor molecules.

4 Results

In Fig. 1a, we show the simulated H_2O and CH_4 trends for the 1980s, a period with strongly increasing atmospheric CH_4 and CFC emissions. The combined increase of CH_4 and CFC levels leads to a substantial stratospheric water increase of up to 0.27 ppm/decade at 1 hPa (black lines), which is more than just the transfer of the tropospheric CH_4 trend (green lines). The reduction and even reversal of the CH_4 trend at higher altitudes clearly demonstrates that the oxidation of CH_4 has become more efficient due to the anthropogenic CFC emissions. This process was previously studied by Nedoluha et al. (1998), who also found increased oxidation of CH_4 by Cl due to increasing CFC emissions. However, the conclusion from their modelling study over five years was that this effect should be small.

When we also include a decadal increase of water vapour input from the tropopause of 0.5 ppm, which equals the average trends from all available measurements (Rosenlof et al., 2001), the corresponding increase in OH results in further conversion of CH_4 to H_2O (blue lines in Fig. 1). Finally, a

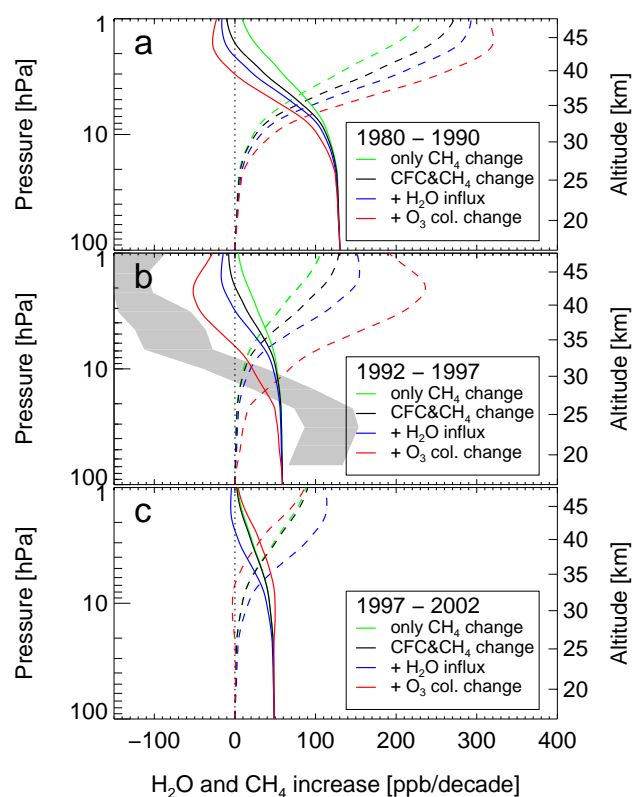


Fig. 1. Box model calculations illustrating the effect of increasing CH_4 and CFC levels in the atmosphere, increasing input of water from the troposphere to the stratosphere and a change of the upper stratospheric ozone column on water levels in the stratosphere for the period of the 1980s (a), 1992–1997 (b), and 1997–2002 (c). Solid lines show the CH_4 trends and dashed lines the H_2O trends over the respective periods. The additional H_2O input from the troposphere of 500 ppb/decade (for the blue and red dashed lines) is subtracted for better reading. In (b), the observational CH_4 data from (Randel et al., 1999) are shown as grey-shaded area for comparison.

reduction of the upper stratospheric partial ozone column by 5% in the 1–10 hPa region (this value is representative for the 1980s, WMO, 2003) also leads to more efficient oxidation of CH_4 to H_2O , augmenting the trend due to increased Cl and H_2O levels (red lines in Fig. 1). Thus, as argued above, all three chemical effects cause an intensified CH_4 oxidation in the stratosphere, leading to a significant increase of upper stratospheric water levels. Since many of the chemical reaction rate coefficients are temperature dependent and stratospheric temperatures have changed over the periods considered here, we carried out sensitivity tests to examine the effect of changing temperatures on the presented model results. For a trend of 2 K/decade, which is at the upper limit of observational values (WMO, 2003), the effect of the temperature changes was about 10 ppb/decade, i.e. at least one order of magnitude smaller than the combined chemical effects.

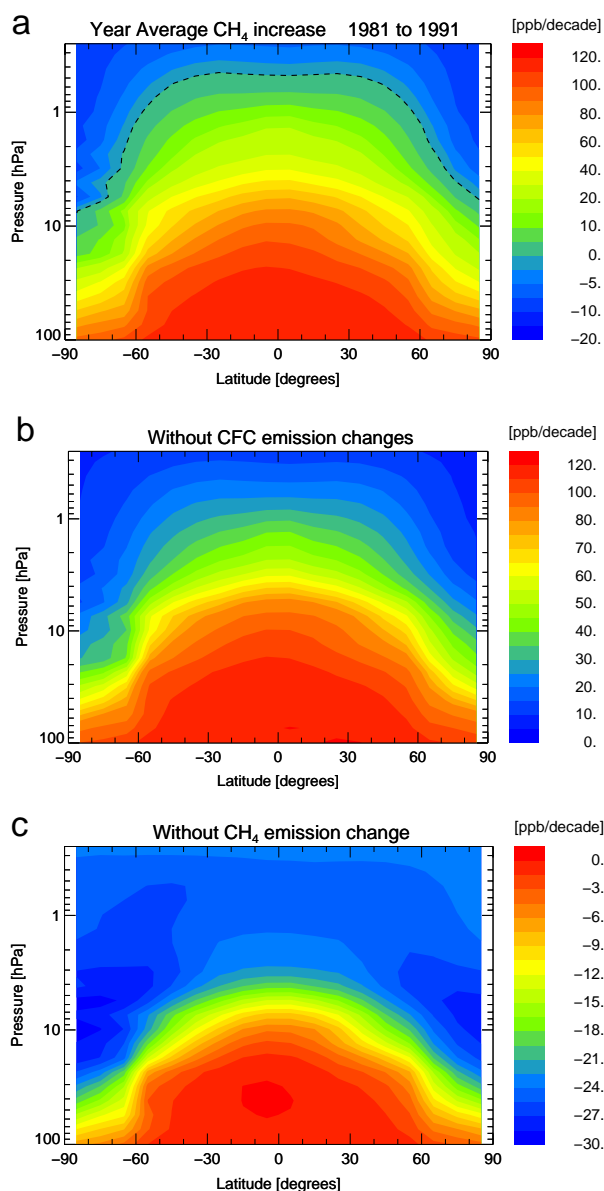


Fig. 2. Results from the Mainz photochemical 2-D model show the latitude dependence of the CH₄ trends in the stratosphere for the period 1981–1991 (period shifted by 1 year compared to Fig. 1a to avoid initialization biases). Shown are the differences between model simulations performed under atmospheric conditions representative of 1991 and 1981 based on atmospheric observations: Three scenarios were studied: **(a)** changing CH₄ and CFC levels from 1981 to 1991, **(b)** changing only the CH₄ levels and **(c)** changing only the CFC levels.

The box model results are corroborated by 2-D model calculations. Figure 2 shows the latitudinal distribution of the temporal CH₄ trends throughout the stratosphere. In panel (a) we have changed the atmospheric burden of CH₄ and CFCs according to the available observations. In panels (b) and (c) the CFC and CH₄ changes, respectively, are switched off. Figure 2b shows that without more efficient oxidation

of CH₄, i.e. without changes in atmospheric CFC levels, the simulated CH₄ trends are positive throughout the stratosphere, a result which is driven by the tropospheric increase of CH₄. The temporal trends decrease with increasing residence time in the stratosphere since CH₄ is increasingly removed (and thus also the additional input from the troposphere). Figure 2c shows results from simulations where tropospheric CH₄ levels were kept constant, and only the CFC increase was considered. The modelled trends are now negative throughout the stratosphere due to more efficient CH₄ oxidation by Cl. Figure 2a shows that when both effects are considered, the general trends are similar to the box model results: CH₄ trends switch from positive to negative because the input of CH₄ from the troposphere is increasing and because CH₄ is more efficiently oxidized to H₂O throughout the middle and upper stratosphere when its removal rate is enhanced by higher CFC levels. The overall trends are slightly smaller for the 2-D model results than for the box model results, and so in the box model simulations CH₄ trends change sign at an altitude slightly higher than deduced from the box model simulations. We note that in the 2-D model only the effects due to the increase of CH₄ and Cl levels (and the corresponding ozone depletion, which is calculated self-consistently) are considered; solar cycle effects on O₃ and the increase of H₂O input from the troposphere are not included. Based on the box model results, including the latter effect would bring the results from the two models into even better agreement. The 2-D simulations also show that the modelled trends depend only moderately on latitude, which confirms that the box model calculations at 15° N can be taken as representative for a greater latitude range.

Global satellite observations of stratospheric water vapour from the HALOE instrument became available in late 1991. We now consider the period 1992 to 1997, for which a strong increase in upper stratospheric H₂O trends with altitude was reported based on HALOE data (Randel et al., 1999). The period of 1992 to 1997 was characterized by a decrease in the tropospheric CH₄ growth rate (Dlugokencky et al., 1994) and a decline in CFC emissions as a consequence of the Montreal protocol (WMO, 2003). Further, global ozone observations from the HALOE and SAGE II instruments show a strong decline in upper stratospheric ozone. This is likely a solar cycle effect (WMO, 2003) since it happened during the declining phase of the solar cycle, but it has also been associated with the eruption of Mount Pinatubo in 1991 (Randel et al., 1999). For our simulations we use the annual average of HALOE O₃ measurements at 15±5° N, the latitude of our box model simulation, from 1992 and 1997, which show a decrease of 3–4% between 5 and 0.1 hPa. The results show that H₂O production from the increase of CH₄ and CFCs alone was much smaller during that period than during the 1980s (Fig. 1b). However, the large change in the O₃ column more than compensates for the reduced chlorine and CH₄ increase, and the additional oxidation of CH₄ is even stronger than in the 1980s.

Thus, the altitude dependence of the trends from 1992 to 1997 which were observed in the stratosphere (Randel et al., 1999) is reproduced in the model results shown in Fig. 1b: CH₄ trends decline and even turn negative at high altitudes and H₂O trends slowly increase with altitude. The chemical changes discussed here can account for about 50% of the observed atmospheric CH₄ trends (Fig. 1b). The most important contributor to the trends from 1992 to 1997 is the decline in upper stratospheric ozone. This also implies that the HALOE derived H₂O trend during the early 1990s was biased by solar cycle related variations in atmospheric ozone changes in a manner not recognized previously. This finding is supported by investigations of longer HALOE time series, which generally show smaller temporal trends (Rosenlof, 2002).

Over the years 1997–2002, the increase in upper stratospheric H₂O as observed by HALOE was negligible (Rosenlof, 2002; Nedoluha et al., 2003). We also investigated the chemical changes for this period. Since the period 1997–2002 was within an increasing phase of the 11 year solar cycle, upper stratospheric O₃ increased and we use an increase of 1–3% between 5 and 0.1 hPa, derived from the HALOE data. Owing to the regulations under the Montreal protocol, the stratospheric chlorine loading was almost unchanged (WMO, 2003). Figure 1c shows that there is indeed no effect due to CFC emissions, but the global increase of tropospheric CH₄ mixing ratios still caused H₂O mixing ratios to increase in the upper stratosphere. This is augmented by increased water input from the troposphere, while the increase of the O₃ column now actually diminishes the increase of H₂O. In combination, all effects together produce only a small increase of up to 80 ppb/decade, thus 40 ppb over the 5 year period. This is less than in the earlier periods, in agreement with the observations, which do not show a significant trend for H₂O in the period 1997–2002.

5 Future development of stratospheric H₂O trends

The model results presented above show that anthropogenic CFC emissions, the resulting thinning of the upper stratospheric ozone column as well as the chemical effect of increased water input from the troposphere have led to a significant increase in middle and upper stratospheric water at a given altitude since the 1980s. Further, solar cycle effects have a strong impact, and have partly masked the long-term trends in the 1990s, the first decade of global satellite observations. It is predicted that with the regulations of CFCs under the Montreal protocol, chlorine levels in the stratosphere will decrease further in the future, and that the ozone depletion will slow down and will eventually reverse (WMO, 1999, 2003). Figure 3 shows box model predictions for upper stratospheric water trends from 2000 to 2050. In these calculations we have assumed future stratospheric chlorine levels based on the WMO halocarbon baseline scenario (Table 4B-3

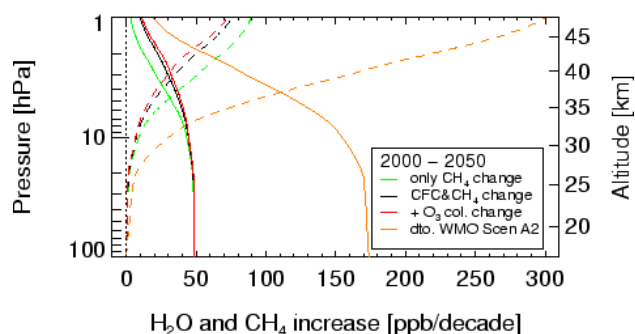


Fig. 3. Future scenario for the increase in stratospheric water vapor taking into account projections for CH₄ increase, the decrease in stratospheric chlorine and the recovery of stratospheric ozone. Solid lines show the CH₄ trends and dashed lines the H₂O trends. The green, black and red lines depict the individual effects (colours correspond to Fig. 1) calculated for a projected CH₄ increase according to the WMO baseline scenario (Table 12.2 in WMO, 1999). The orange line is the final result (i.e. corresponding to the red line) for a CH₄ increase according to WMO scenario A2 (Table 4B-3 in WMO, 2003).

in WMO, 2003). Also tropospheric CH₄ mixing ratios follow the WMO baseline scenario (Table 12.2 in WMO, 1999), i.e. they increase to 2000 ppb in the year 2050. The ozone profiles used come from a 2-D model simulation driven by these scenarios. The results show that primarily the assumed continuing increase of atmospheric CH₄ will cause upper stratospheric water levels to increase further (Fig. 3). In contrast to the conditions in the 1980s, the decline in chlorine and the recovery of stratospheric ozone will reduce the increase of H₂O, i.e. they cause a less efficient conversion of CH₄ to H₂O in the future. Since the future CH₄ increase is difficult to predict (Simpson et al., 2002), this important contribution to the H₂O trends is uncertain: The orange lines in Fig. 3 show the results employing alternatively the WMO scenario A2 (Table 4B-3 in WMO, 2003) with an increase of tropospheric CH₄ to 2562 ppb in 2050. Also, the future development of the input of tropospheric water into the stratosphere is very speculative and is therefore not included in the prediction, and neither is the possible impact of a future hydrogen economy as a potential additional source of stratospheric water, as discussed recently (Tromp et al., 2003).

6 Conclusions

Increases in the stratospheric abundance of stratospheric abundances of Cl, O(¹D) and OH due to anthropogenic CFC emissions, the thinning of the stratospheric ozone column and increasing input of water from the troposphere to the stratosphere have led to enhanced chemical conversion of CH₄ to H₂O in the past decades. Clearly, the more efficient oxidation of CH₄ as described here cannot explain the observed increase in the quantity H₂O+2×CH₄ in the

stratosphere. Likewise, this chemical mechanism is unlikely to cause large interannual and spatial variability in the trends, and we expect that this variability may be caused by dynamical changes (Considine et al., 2001; Rosenlof, 2002). Nevertheless, the comparison of model simulations and observations indicates that approximately 50% of the observed enhanced oxidation of CH₄ in the stratosphere can be attributed to chemical changes. Thus, these chemical changes, which are based on reliable atmospheric observations and well-established chemical reaction mechanisms, have to be taken into account when stratospheric water vapour trends are analysed. We conclude that this chemical mechanism constitutes an important contribution to the explanation of the total stratospheric water trends.

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